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Abstract:

CO_2 capture and sequestration represent a major industrial and scientific challenge of this century. There are different methods of CO_2 separation and capture, such as solide adsorption, amines adsorption and cryogenic fractionation. Although these processes are well developed at industrial level, they are energy intensive. Hydrate formation method is a less energy intensive and has an interesting potential to separate carbon dioxide (Nguyen Hong, 2007). Gas hydrates are crystalline compounds that consist of an hydrogen bonded network of water molecules traping a gas molecule. Gas hydrate formation is favoured by high pressure and low temperature. In this work we present a computer program GasHyDyn based on Van der Waals and Plateeuw model. This program allows the estimation of thermodynamic equilibrium conditions. Experimental equilibrium data of CO_2-CH_4 and CO_2-N_2 mixtures are presented and compared to theoretical results given by the GasHyDyn software.

Keywords:

gas hydrate ; thermodynamic, CO_2 ; phase equilibrium

I. Introduction to thermodynamic modelling

Gas hydrate formation and dissociation is studied for long times. The industrial application of this process requires knowledge of formation and dissociation pressure and temperature to define the thermodynamic limits of CO_2 capture process. Most of the thermodynamic models for the prediction of hydrate formation or dissociation conditions are modifications of Van der Waals and Platteeuw model (Van der Waals, 1959).

Van der Waals and Platteeuw model is based on the equality between water chemical potentials in the liquid phase and in the hydrate phase. The hydrate phase *s* is described with statistical thermodynamics and derived on the basis of the assumption of the similarity between gas capture within the hydrate structure, composed of cavities, and isothermal adsorption based on the Langmuir isotherms. Van der Waals and Plateeuw treated hydrate cages as adsorption sites in which species become adsorbed or encaged. The mechanisms of the two processes are, however, quite different. The liquid phase is described with the classical thermodynamic, especially with the Gibbs Duhem relation. For these two phases, the components fugacity in gas phase must be evaluated with the equation of state. Several equations can be used like, Soave-Redlich-Kwong, Peng-Robinson and Patel-Teja equations of state.

In some cases, the liquid phase is not ideal (high solubility of gas in the liquid phase or addition of inhibitors). Therefore, it is necessary to calculate the activity coefficients to quantify the deviation from ideal state and the most used models are NRTL and UNIFAC.

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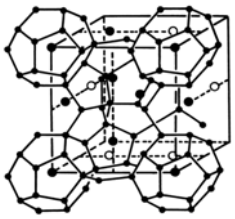
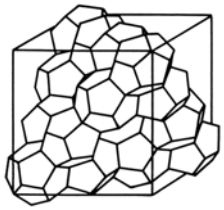
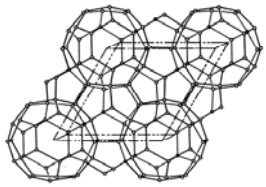
This work presents an experimental study on thermodynamics of gas hydrate formation. The equilibrium results obtained from experiments have been validated by the Van der Waals model throw a software called GasHyDyn developed by our group.

I.1. Hydrate structures

The clathrates are ice-like compounds in the sense that they correspond to a re-organisation of the hydrogen links to form a solid in which the crystallographic structure is based on these links. The clathrates of water are also qualified improperly of "porous ice" because the water molecules build a solid network of cavities in which could be captured gases, volatile liquids or other small molecules.

The gas hydrates can exhibit three different structures called SI, SII and SH (Sloan, 1997). Each structure is a combination of different types of polyhedron sharing faces between them. Jeffrey (1984) suggested the nomenclature e^f to describe each polyhedron: e is the number of edges of the face, and f is the number of faces with e edges. Currently, three different structures have been established precisely, called I, II and H (Table 1).

Table 1: Structure of gas hydrates (Sloan, 1998)

	SI		SII		SH		
							
Cavity	5^{12}	$5^{12}6^2$	5^{12}	$5^{12}6^4$	5^{12}	$4^35^66^3$	$5^{12}6^8$
Type of cavity (j: indexation number)	1	2	1	3	1	5	4
Number of cavity (m_j)	2	6	16	8	3	2	1
Average cavity radius (nm)	0.395	0.433	0.391	0.473	0.391	0.406	0.571
Variation in radius, %	3.4	14.4	5.5	1.73			
Coordination number	20	24	20	28	20	20	36

I.2. Van der Waals and Platteeuw model

Van der Waals and Platteeuw model describes the hydrate phase throw statistical thermodynamics and is based on the following assumptions (Chen, 1996):

- Each cavity contains at most one guest (gas) molecule
- The interaction between guest and water molecules can be described by a pair potential function of the pair gas-molecule, and the cavity can be treated as perfectly spherical.
- The free energy contribution of the water molecules is independent of the modes of occupancy of guest molecules, this assumption means that the gas molecules don't deform cavities.
- There is no interaction between the guests molecules in different cavities, gas molecules interact only with the nearest water molecules.

From the previous hypotheses, the statistical thermodynamics allows the description of the different parameters of the system and link them to quantities like temperature, volume and chemical potential.
In the case of hydrates, at thermodynamic equilibrium, we can write the equality of chemical potentials of water in the liquid phase and in the hydrate phase. This relationship can be rewritten regarding to a reference state. For the hydrate, the reference state used in the Van der Waals and Plateeuw model is a hypothetical phase β which corresponds to the empty cavities.

$$\Delta\mu_w^{\beta-H} = \Delta\mu_w^{\beta-L} \quad (1)$$

$\Delta\mu_w^{\beta-H}$ is the difference of chemical potential between water in hydrate phase and in reference phase β as follows Chen (Chen, 1996)

$$\Delta\mu_w^{\beta-H} = RT\sum_i \nu_i \ln(1-\sum_j \theta_j^i) \quad (2)$$

ν_i is the number of cavities of type i per mole of water (see Table 1). θ_j^i is the occupancy rate of the cavities of type i by the gas molecule j. This parameter is very important to define thermodynamic equilibriums and to determine hydrate properties.
The occupancy rate is determined by analogy between the hydrate formation and the Langmuir adsorption (Sloan, 1998). The assumptions of Langmuir adsorption are:

- The guest molecule is at adsorbed at the surface.
- The adsorption energy is independent from the presence of other adsorbed molecules.
- The maximum amount of adsorption corresponds to one molecule per site.
- The expression of θ_j^i is:

$$\theta_j^i = \frac{C_j^i f_j(T,P)}{1+\sum_j C_j^i f_j(T,P)} \quad (3)$$

Equation 2 can be written as:

$$\Delta\mu_w^{\beta-H} = RT\sum_i \nu_i \ln(1-\sum_j C_j^i f_j(T,P)) \quad (4)$$

C_j^i is the Langmuir constant of component j in cavity i, it describes the potential interaction between the encaged guest molecule and the water molecules surrounding it. It is evaluated by assuming a spherically symmetrical cage and can be described by a spherical symmetrical potential:

$$C_j^i = \frac{4\pi}{kT}\int_0^R \exp\left(\frac{-w(r)}{kT}\right) r^2 dr \quad (5)$$

w is the interaction potential between the cavity and the molecule according to the distance r between the molecule and the cavity wall. The interaction potential is determined with several models: Van der Waals and Plateeuw model (1965), Parrish and Prausnitz model (1972) and the Kihara model that is the most precise (McKoy, 1963).
Parrish and Prausnitz model (Parrish, 1972) proposed a simplified expression of Langmuir constant:

$$C_j^i = \frac{A_j^i}{T}\exp\left(\frac{B_j^i}{T}\right) \quad (6)$$

where A and B are constants, given in the literature by Munk *et al* (1988) and given in the following table.

Table 2: Where A and B are constants, given in the literature by Munk et al (1988)

Component	Structure	Small cavities		Large cavities	
		A[K/atm]	B[K/atm]	A[K/atm]	A[K/atm]
CH_4	I	$7.228 .10^{-4}$	$3.187 .10^{3}$	$2.335 .10^{-2}$	$2.653 .10^{3}$
	II	$2.207 .10^{-4}$	$3.453 .10^{3}$	10^{-1}	$1.916 .10^{3}$
CO_2	I	$2.474.10^{-4}$	$3.41 .10^{3}$	$4.246 .10^{-2}$	$2.813 .10^{4}$
	II	$8.45 .10^{-5}$	$3.615 .10^{3}$	$8.51 .10^{-1}$	$2.025 .10^{3}$
N_2	I	$1.617 .10^{-3}$	$2.905 .10^{3}$	$6.078 .10^{-3}$	$2.431 .10^{3}$
	II	$1.742 .10^{-4}$	$3.082 .10^{3}$	$1.8 .10^{-2}$	$1.728 .10^{3}$

Détermination of $\Delta\mu^{\beta-L}$

The chemical potential of water in the aqueous phase is calculated with the classical thermodynamics from the Gibbs Duhem relation which gives the free enthalpy variation with temperature and pressure. The reference conditions are the temperature T_o = 273.15 K and the pressure P_o = 0. The difference of chemical potential of water between the liquid phase and the hypothetical β phase can be written (Ballard, 2001):

$$\left(\frac{\Delta\mu_w}{RT}\right)_{T,P} = \left(\frac{\Delta\mu_{w0}}{RT}\right)_{T0,P0} - \int_{T0}^{T}\frac{\Delta h_w}{RT^2}dT + \int_{P0}^{P}\frac{\Delta V_{w0}}{RT}dP - \ln(\gamma_w * X_w) \quad (7)$$

with

$$\Delta h_w = \Delta hw_0 + \int_{Tref}^{T}\Delta Cp dT \quad (8)$$

$$\Delta Cp = \Delta Cp_0 + a(T - T_0) \quad (9)$$

From Equations 7, 8, and 9 the computation of the difference of potential of water between the liquid phase and the β phase requires firstly the determination of the reference conditions $\Delta\mu_{wo}$, ΔCp_o, Δh_{wo}, a and ΔV_{wo}. The value of ΔVw_o is determined by x-ray diffraction (Von Stakelberg, 1951), $\Delta\mu w_o$, ΔCp_o, Δhw_o, and a were determined from experiments (Sloan, 2008), one of the usual methods was proposed by Holder (Holder, 1980). Secondly the calculation of the gas fugacity (for example by using an equation of state) and thirdly the evaluation of the gas solubility (Thiam, 2008). Also, in the case of the presence of inhibitors or highly soluble gas or salts, equation 7 requires the evaluation of the activity coefficient (γ_w) of water by a model NRTL or UNIFAC.

Table 3. Reference properties of hydrates from Sloan (1998)

	Unit	Structure I	Structure II
$\Delta\mu w_0$	J/mol	1263	838.8
Δhw_0 hydrate/ice	J/mol	1389	1025
Δhw_0 hydrate/liquid water	J/mol	-4622	-4986
ΔV_{wo} hydrate/ice	m3/mol	0.0000029959	0.00000339644
ΔV_{wo} hydrate/liquid water	m3/mol	0.0000045959	0.00000499644
ΔCp_0 hydrate/ice	J/(mole.K)	3.315	1.029
a hydrate/ice	J/(mole.K.K)	0.121	0.00377
ΔCp_0 hydrate/liquid water	J/(mole.K)	-38.12	-38.12
a hydrate/liquid water	J/(mole.K.K)	0.141	0.141

But in the specific case of pure water, activity coefficient of water is 1. The molar fraction of gases is correlated from Holder (1980).
The solubility of gases is given by

$$x = h\frac{f(T,P)}{\exp\left(\frac{PV^{\infty}}{RT}\right)} \quad (10)$$

with V^{∞} =32 $cm^3.mol^{-1}$

h (Pa^{-1}) is Henry constant, it is calculated by the following correlation (Holder 1980)

$$\frac{1}{h} = \exp\left(A + \frac{B}{T}\right) \quad (11)$$

A and B are constants given in table 4

Table 4: Constants for Henry constant calculation (Holder 1980)

Gas	A	B
CO_2	14.283146	-2050.3269
N_2	17.934347	-1933.381
CH_4	15.826277	-1559.0631

I.3. GasHyDyn Software

GasHyDyn is a software developed by St-Etienne School of Mines, based on Van der Waals and Plateeuw model for the prediction of gas hydrate equilibriums with the constant of Parrish and Prausnitz. This program predicts the thermodynamics and the cage occupancy of stable hydrate structures (SI, SII and SH) from a given pressure or temperature and composition of each gas in a mixture:
(http://www.emse.fr/fr/transfert/spin/depscientifiques/GENERIC/hydrates/logiciel_jmh/GasHyDyn.html).
This software can also be used for pure gas hydrates. The software allows takes in account constants ΔVwo, $\Delta \mu wo$, ΔCpo, Δhwo, and a from different authors.

II. Materials and Methods

An experimental apparatus (Figure 1) has been built to investigate thermodynamic equilibrium of hydrates while an experimental procedure was established to determine composition of gas, liquid and hydrate phase. In the present study, experiments of gas hydrate formation were carried out to separate CO_2 from CO_2-CH_4 and CO_2-N_2. The experimental results have allowed the determination of hydrate formation conditions. The experimental set-up is a classical batch reactor composed of a Pyrex cylinder that is filled with a volume of 800 mL to 1 L of water and an anionic tracer ($LiNO_3$). This cell is located in the stainless steel autoclave in which the pressure can be raised up to 10 MPa. The autoclave is surrounded by a cooling jacket. Two sapphire windows mounted on both sides of the reactor make possible observation of hydrates. A four vertical-blade turbine impeller ensures stirring of the suspension during crystallization. Temperature is monitored by a Pt100 probe (with an accuracy equal to ±0.15°C) in the bulk and pressure is measured by mean of a pressure transducer (range: 0–10 MPa with an accuracy equal to ±0.05 bar). The data acquisition unit (P, T) is connected to a personal computer. The composition of the gas phase is determined using gas chromatography (with accuracy equal to 2.2%).
Gas sampling is performed by a ROLSI instrument. This tool collects a controlled volume of gas (some μm^3) which is directly injected in the loop of a gas chromatograph (VARIAN model CP-3800 GC). A classical valve is used to take a 1ml liquid sample which is directed to

DIONEX ionic chromatography to measure the tracer ($LiNO_3$) concentration (the tracer is an ionic element which is not incorporated in the hydrate structure but concentrated in the liquid phase during crystallization).

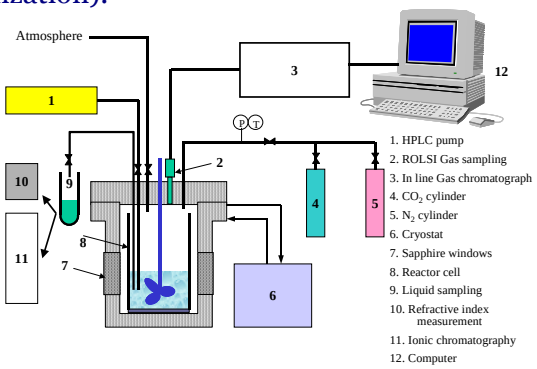


Figure 1: Experimental apparatus

The hydrate is obtained by crystallization of a gas mixture (CO_2-CH_4 or CO_2-N_2) with a liquid phase (water + tracer ($LiNO_3$)). At the beginning, the reactor and its loading lines are vacuumed. The cell is first loaded with the gas mixture to reach the operative pressure. The reactor is cooled down to a temperature, low enough to form hydrates. First temperature increases due to gas compression and then the temperature decreases to reach operative temperature. As the system reaches a constant temperature and a constant pressure, 800 ml-1000 ml of liquid (water + tracer) at ambient temperature is injected by using the HPLC pump. A temperature increase and a pressure increase are simultaneously observed due to the "high" temperature of the liquid mixture and due to gas compression followed by a pressure drop due to gas dissolution. After some hours, suddenly the temperature increases which characterizes the beginning of nucleation and crystallization. During exothermic crystallization gases are consumed and at the end of the crystallization the temperature slowly returns to the operative condition.

III. Experimental results

To establish phase diagrams for CO_2-CH_4 mixture at 4°C and for CO_2 - N_2 mixture at 2.7°C an experimental work was made. Figures 2 and 3 show the phase diagrams between gas phase and hydrate phase obtained from experiment for each mixture.
These results were compared to the van der Walls and Plattteuuw model with constants from Sloan (Sloan, 1998). The GasHyDyn software was used to calculate the equilibrium points. There is a good agreement between model and experiment.

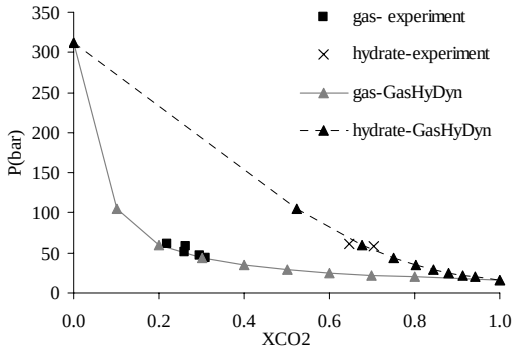


Figure 2: Gas- hydrate phase diagram for CO2-N2 mixture at 2.7°C

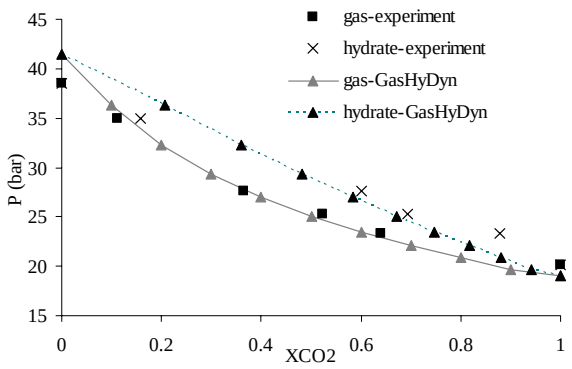


Figure 3: Gas- hydrate phase diagram for CO2-CH4 mixture at 4°C.

IV. Conclusion

In this work two different gas mixtures (CO_2-CH_4 and CO_2-N_2) have been studied. For both mixtures experimental results show the feasibility of gas separation to decrease the operative pressure during crystallization of CO_2.
The software GasHyDyn was used to calculate the equilibrium points for mixtures from the model of van der Waals, Plateweeuw with Kihara parameters. These calculations were compared to experiments with a good agreement. These conclusions validate the experimental set-up and procedure. Also this work has permitted us to test GasHyDyn software to put it now available in internet.

Nomenclature

T	temperature [K]	ε	maximum attraction potential [-]
ν_i	number of cavities of type i per water moles [-]	z	cavity coordination number [-]
θ^i_j	occupation rate of cavity i and gas j [-]	a	spherical nucleus radius [m]
Pf	pressure [Pa]	σ	distance between to molecules for null potential [m]
r	distance between the molecule and the cage [m]	γ_w	water activity coefficient [-]
R	gas molecule radius [m]	X_w	molar fraction of water in the liquid phase [-]
k	Boltzmann constant [$J.K^{-1}$]	$a_{w,H}$	water activity in hydrate phase [-]

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